Thin Film Arresters Obtained by Metal Evaporation

J. Ziaja
Institute of Electrical Engineering Fundamentals of the Wroclaw University of Technology
50-370 Wroclaw, Poland

***Abstract-* Ceramic varistors based on zinc oxide have been shown to have excellent properties as protection devices used in power industry. However their breakdown voltage, dependant on number of grain boudaries, is too high for use in electronic applications. In this article performace of micro-devices having varistor-type current-voltage (I-V) characteristics with low breakdown voltage is reported.**

I. INTRODUCTION

Oxide varistors are mainly manufactured using ceramic technology. Powdered metal oxides: ZnO making the matrix, Bi_2O_3 and, in small amounts, other metal oxides as Al_2O_3, Co_3O_4 and MnO_2 are mixed together, pressed into pellets and then sinterred. Mass varistors obtained this way have highly non-linear current-voltage (I-V) characteristics. The shape of the varistor I-V characteristics is determined not only by the bulk material chemical composition but also by parameters of its thermal treatment [1]. In the microstructure of varistor ceramics three main constituents may be distinguished: semiconducting grains of ZnO, a matrix of intergranular insulating phase, rich in bismuth and junctions between grains and the intergranular phase. The research points out to the fact, that the junctions formed on the border between ZnO grains and the intergranular phase are responsible for a potential barrier rise, which controll the current flow through the bulk of the ceramics [2, 3]. The breakdown voltage of varistors produced using ceramic technology is then dependant not only on the breakdown voltage of a single junction but also on the number of, connected in serial, junctions situated across the thickness of the device. Applications of the varistors in protection of fragile electronic circuits demand sufficiently low value of the breakdown voltage but this is impossible to attain when using classical ceramic technology. Such prospects are however created by thin-film technologies, making it possible to obtain layers with thickness comparable to the size of a single grain of ZnO [4-7]. These techniques are also compatible with processes utilised in microelectronic industry thus enabling incorporation of thin-film varistors in LSI circuits and gas sensors. Zn-Bi-O thin films prepared by magnetron sputtering exhibit H_2 sensitivity [8] and could be used in gas sensors.

II. EXPERIMENTAL

The specimens were prepared as a two-component Zn-Bi system. Zinc and bismuth, 92% and 8% by weight respectively, were subjected to a calcination. The material prepared in this way was then deposited by thermal evaporation onto carefully cleaned and polished substrates made of a nickel sheet. This metal substrate served also the purpose of one of the electrodes in subsequent measurements of the electrical properties. The evaporation process was carried out using 99.99% purity materials in $p=10^{-3}$ Pa vacuum. The substrates were then machine cut into pieces having dimensions of 5 by 10 mm. Samples were placed in the oven and hold at a temperature of 400 °C for 5 hours in order to oxidise Zn-Bi layer. This process was followed by annealing phase when the temperature was risen up to 800 °C to obtain structures having various grain size distribution thus various electrical properties. Finally the second electrode was deposited at the top of a thin-film varistor device by means of a silver target RF sputtering.

Microstructure of the specimens was investigated using SEM (Scanning Electron Microscopy) and X-ray microprobe. Their electrical properties were measured by means of a computerised set-up with Keithley 617 electrometer.

III. RESULTS AND DISCUSSION

Fig. 1 shows I-V characteristics of ZnO- Bi_2O_3 structures obtained by means of a pure metal evaporation as well as the effect of the annealing temperature variation. For low temperatures, not exceeding 700 °C, I-V characteristics not exhibit varistor type of behavior. Increase of the annealing temperature results in the nonlinear I-V dependence. In low voltage range, up to app. 3 V, the current-voltage dependence is strictly ohmic. In higher voltage range, above the threshold value (equal to the breakdown voltage) the I-V characteristics starts to bent and the current-voltage dependence becomes nonlinear and well described by $I=f(V^{\alpha})$ type function

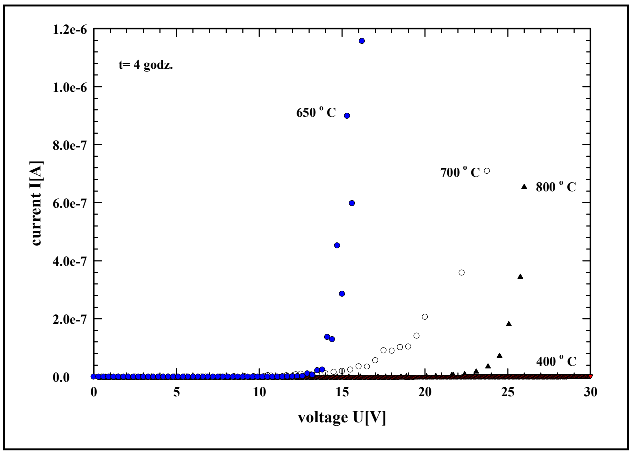

Figure 1. I-V characteristics of ZnO- Bi_2O_3 structures deposited by means of thermal evaporation, annealed at different temperatures.

It may be attributed to the thermally stimulated change of the mean grain size, which becomes evident when observing Fig. 2, showing exemplary SEM scans of the varistor structures.

Fig. 2 Structure of $ZnO\text{-}Bi_2O_3$ layers deposited on corundum substrate, annealed at 800 ^{o}C.

Fig. 3 shows results of X-ray diffraction analysis (XRD) using CuKα radiation. It can bee seen from Fig. 3, that - for films annealed at 400 ^{o}C – only background peaks appear. This could bee attributed to amorphous nature of the material. Crystal structures start develops as the annealing temperature increases. XRD spectra for the film annealed at 700 ^{o}C shows new peaks at diffraction angle $2\Theta=20^o - 35^o$, which is correlated to crystal phase formation. XRD spectra for the film annealed at 800 oC shows high intensity peaks at the same diffraction angle ($2\Theta=20^o - 35^o$) and background peaks fading. The most intensive pikes are those attributed to Zn and Bi. It could be attributed to crystal nature of the material.

As the annealing temperature increases, the crystalline nature slowly develop and the films annealed at 800 ^{o}C exhibit strong varistor type of behavior.

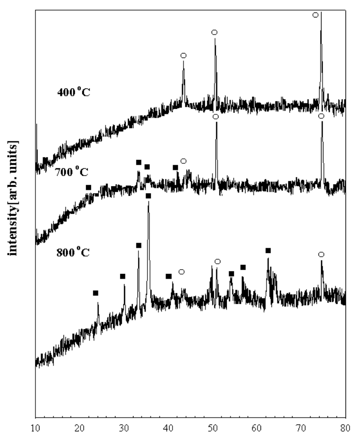

Figure 3. XRD spectra of thermally evaporated thin films of $ZnO\text{-}Bi_2O_3$ annealed at different temperatures.

The thickness of the investigated ZnO- Bi_2O_3 composite layers, estimated on the basis of SEM scans of their fracture, was equal to 8 μm.

IV. Conclusions

The shape of I-U characteristics measured for varistor thin-film structures allows us to conclude that even in such a simple bicomponent system it is already possible to obtain a varistor effect with relatively low breakdown voltage. It is made possible when thermal vacuum evaporation of pure metals is applied as a deposition process. Moreover, controll of the device electrical properties, particularly its breakdown voltage, is possible when the right conditions of the subsequent thermal treatment are selected (temperature and time of annealing and cooling).

References

[1] T. Hozer, Półprzewodnikowe materiały ceramiczne z aktywnymi granicami ziarn, Warszawa, PWN, 1990.
[2] K. Eda, Zinck oxide varistors, IEEE Electrical Insul. Magazine, 1989, Vol. 5, No. 6.
[3] M. Matsuoka, „Nonohmic properties of zinc oxide ceramics", Jpn.J.Appl.Phys., 10 (1971), pp.736-746.
[4] M.W. Barsoum, A. Elkind, Low breakedown varistors by grain boundary diffusion of molten Bi_2O_3 in ZnO, J. Am. Ceram. Soc., 79(4) 962-66 (1996)
[5] T. Nakajima, Y. Suzuoki, T. Mizutani, M. Ieda, H. Fujita, Electrical properties and electroluminescence of ZnO composite thin-film varistors, Proceedings of the 3rd International Conference on Properties and Application of dielectric materials, July 8-12 1991, Tokyo, Japan
[6] N. Horio, M. Hiramatsu, M. Nawata et el. Preaparation of zinc oxide metal oxide multilayered thin films for low-voltage varistos, Vaccum, (4), 179-122, 1998
[7] Y. Suzuoki, A. Ohki, M. Nakagawa, T. Mizutani, M. Ieda, Electrical properties of ZnO Bi_2O_3 thin-films varistors, Advances in Varistors Technology, Ceramics Transaction Volume 3, pp. 338-344,
[8] M. Jaroszewski; "Hydrogen influence on properties of thin film arresters", EEEIC Conference on Environment and Electrical Engineering, 5-10 May 2008, in press